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Star-configured carbazole as an efficient near-ultraviolet emitter and hole-transporting material for organic light-emitting devices

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A novel organic material, 9-methyl-1,3,6,8-tetraphenyl-carbazole (MTPC-Me), for use in organic electroluminescent devices has been developed. This star-configured carbazole gives a strong near-ultraviolet (n-UV) emission (λ_{max}=389 nm) with a high emission quantum efficiency of 47% and a narrow full width half maximum of 40 nm. Two types of high-performance organic light-emitting devices were obtained using MTPC-Me as a n-UV emitter and hole-transporting material with maximum external quantum efficiency, brightness, and turn-on voltage of 1.2%, 1040 cd/m^2, and 3.5 V for the former and 1.1%, 18 000 cd/m^2, and 2.4 V for the latter, respectively. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2841063]

The performance of red-to-blue organic light-emitting devices (OLEDs) has improved dramatically over the past decade.[1–4] However, extending OLED emission into the ultraviolet (UV) or near-ultraviolet (n-UV) wavelength is still challenging, despite the useful applications of n-UV OLEDs as an excitation light source for red-to-blue or white luminescence conversion and in high-density information storage devices. In addition, UV or n-UV emitters are widely used as a host material for triplet dopant emitters in phosphorescent OLEDs.[5,6] To date, only several n-UV emitters, such as 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP),[7] *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)(1,10-biphenyl)-4,4′-diamine (TPD),[8,9] and bi(9,9-diaryl-fluorene)s,[10] have been proven to be effective UV or n-UV emitters for OLEDs.

Functionalized carbazoles have played an important role in OLEDs as a host material[11,12] and hole-transporting material (HTM).[13,14] Here, we report efficient n-UV emission with narrow full width half maximum (FWHM) from a novel 1,3,6,8-substituted carbazole derivative, 9-methyl-1,3,6,8-tetraphenyl-carbazole (MTPC-Me), the structure of which is shown in Fig. 1. Two types of high-performance OLEDs have been fabricated by using this star-configured MTPC-Me carbazole as a n-UV emitter and HTM.

The preparation method of MTPC-Me will be described elsewhere. The characteristic data of this compound are as follows: mp, 236.2 °C; MS-EI(*m*/*e*), 485 (M^+, 100.00%), 486 (30%), 243 (15%); elemental analyses: calculated percentage for $C_{37}H_{27}N$: C 91.51%, H 5.60%, N 2.88%; found: C 91.20%, H 5.56%, N 2.68%; ^{1}H NMR($CDCl_3$,500 Hz) δ: 2.94(3H,*s*), 7.38–7.42(4H,*m*), 7.47–7.52(8H,*q*), 7.60–7.65(2H,*m*), 7.80–7.81(4H,*t*), 8.42–8.42(2H,*d*). Three different types of OLEDs were fabricated:

device A: indium-tin oxide (ITO)/MTPC-Me (50 nm)/Alq_3 (50 nm)/LiF (0.5 nm)/Al (100 nm), device B: ITO/NPB (50 nm)/Alq_3 (50 nm)/LiF (0.5 nm)/Al (100 nm), and device C: ITO/CuPc (30 nm)/MTPC-Me (30 nm)/BCP (10 nm)/Alq_3 (30 nm)/LiF (0.5 nm)/Al (100 nm), where ITO glass is transparent anode; copper(II) phthalocyanine (CuPc) is hole-injecting material; *N*,*N*′-bis(naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) is HTM; 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is hole-blocking material (HBM); and tris-(8-hydroxyquinolato) aluminum(III) (Alq_3) is electron-transporting material (ETM) or emitting material (EM). In this work, all OLEDs were prepared[15,16] on patterned ITO glass with a sheet resistance of 20 Ω/□. All layers of the OLEDs were grown by thermal evaporation under a vacuum of 1×10^{-6} Torr. The device performance was examined using Photoresearch PR-650 and Keithley 2400 source meter. All chemicals were sublimed before use.

We have not been able to obtain crystals of MTPC-Me with quality good enough for single crystal x-ray structure determination. Nevertheless, we have obtained crystals of its analog 9-ethyl-1,3,6,8-tetraphenyl-carbazole (MTPC-Et) and determined its crystal structure. As depicted in Fig. 2, due to the four phenyl groups, MTPC-Et is sterically bulky with a

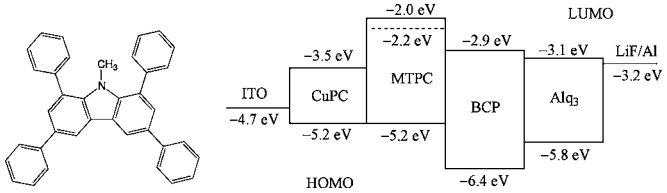

FIG. 1. Chemical structure of MTPC-Me and schematic energy diagrams of organic materials used in this work (HOMO, −5.2 eV; LUMO, −2.2 eV for NPB).

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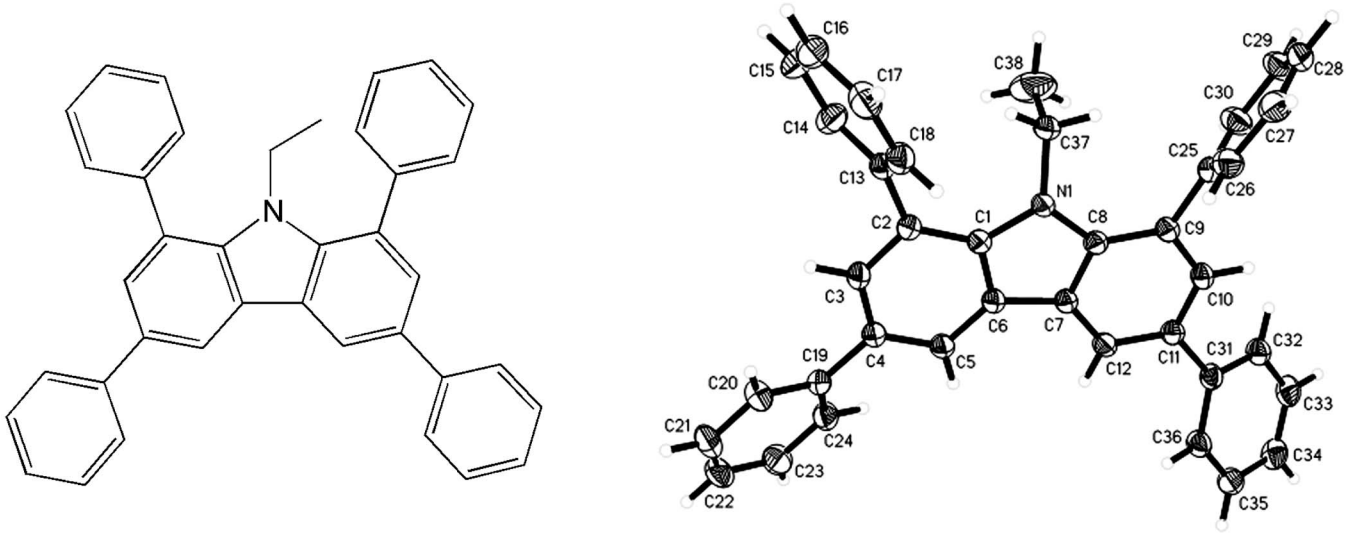

FIG. 2. Chemical structure and crystal structure of MTPC-Et.

star-configured structure and this is essential for this kind of compounds to acquire enough morphological thin-film stability[11–14] and thermal stability. The decomposition temperature and glass transition (T_g) of MTPC-Me was found to be 351 and 220 °C, respectively. The energy levels calculated using cyclic voltammetric data of this compound are shown in Fig. 1. The energy level of the highest occupied molecular orbital (HOMO, −5.2 eV) and lowest unoccupied molecular orbital (LUMO, −2.0 eV) of MTPC-Me are comparable to those of NPB (HOMO, −5.2 eV; LUMO −2.2 eV). With a large band gap of 3.2 eV, MTPC-Me emits a strong n-UV light (λ_{max}=389 nm, decay lifetime=5.3 ns) with a high photoluminescent (PL) quantum efficiency of 47% (quinine in 0.05 mol/l sulfate as standard) and FWHM of 40 nm in CH_2Cl_2 solution, as depicted in Fig. 3. The PL emission of MTPC-Me film (λ_{max}=395 nm) shows a little redshift from that recorded in CH_2Cl_2 solution, presumably this could be attributed to molecular aggregation in the solid state. On the basis of its good thermal and morphological stability, appropriate energy levels, strong n-UV emission, and hole-transporting nature of carbazole-containing compound, MTPC-Me is expected to be a good HTM and EM.

A double-layer device A with MTPC-Me as HTM and Alq_3 as EM and ETM was fabricated. For comparison, a standard device B with a similar structure but using NPB as HTM was also fabricated. Similar to the NPB-based device B, the MTPC-Me-based device A gave a green emission with a peak $|\lambda_{max}|$ at 530 nm, a characteristic of the emission of Alq_3 (Fig. 4), indicating that charge recombination is localized in the Alq_3 layer and MTPC-Me acted primarily as a HTM without causing exciton formation at the interface with Alq_3. This should be attributed to the appropriate HOMO

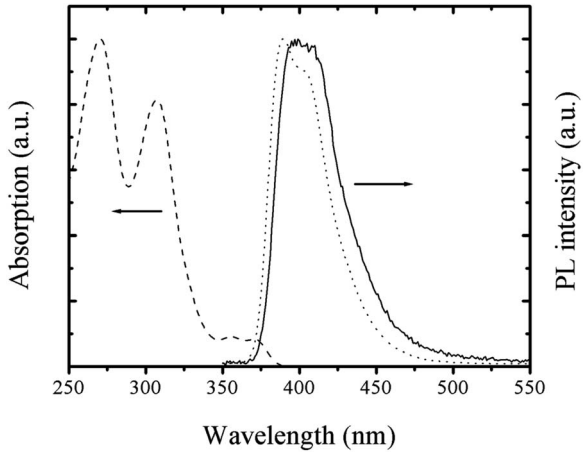

FIG. 3. Absorption (dash line, in CH_2Cl_2) and PL emission (dot line, in CH_2Cl_2; solid line, thin film) spectra of MTPC-Me.

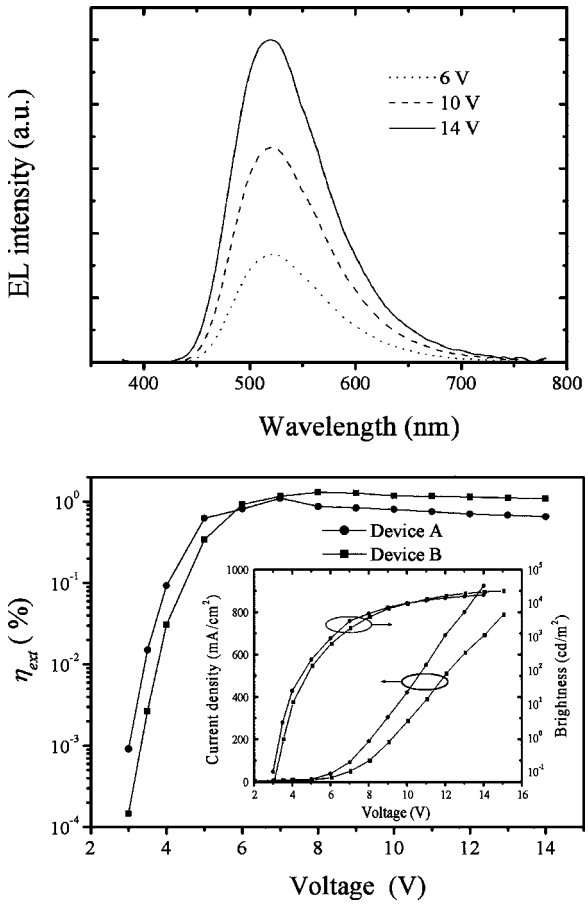

FIG. 4. EL spectrum of device A (top) and external quantum efficiency, current density, and brightness curves (inset) of devices A and B (bottom) vs the applied voltage.

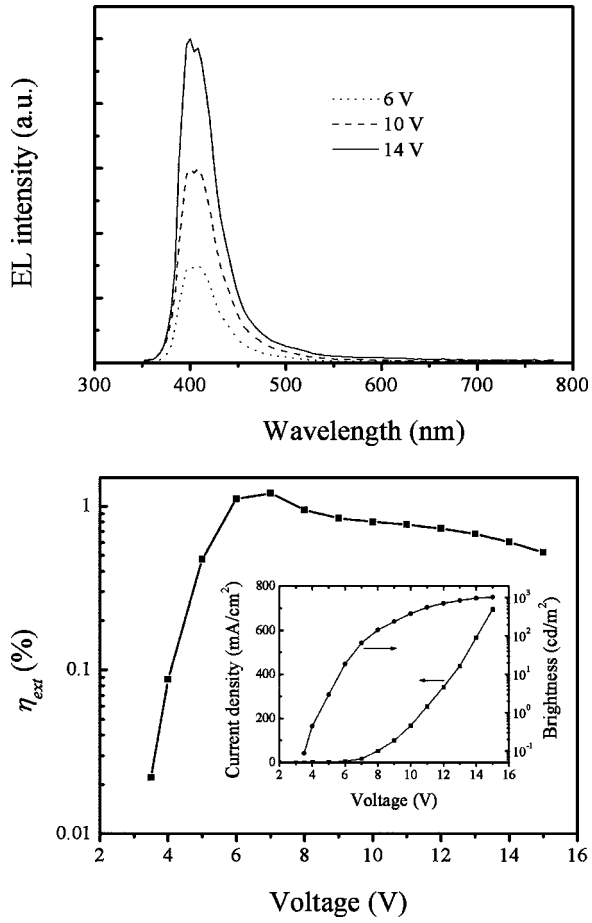

FIG. 5. EL spectrum (top) and external quantum efficiency, current density, and brightness (inset) of device C (bottom) vs the applied voltage.

energy level of MTPC-Me which is favorable for hole injection from ITO to the MTPC-Me and, subsequently, to the Alq_3 layer. Similarly, the appropriate LUMO level of MTPC-Me (a bit higher than that of NPB) blocks electron injection from Alq_3 to itself.[14] The electroluminescent (EL) performance of devices A and B are shown in Fig. 4. Both the current density and luminance of the MTPC-Me-based device A are comparable to that of the NPB-based standard device B (Fig. 4). The maximum external quantum efficiency (η_{ext}), luminous efficiency (η_L), brightness, and turn-on voltage (V_{on}) of the MTPC-Me-based device A are 1.1%, 3.3 cd/A, 18 000 cd/m^2, and 2.4 V, respectively, comparable to the related values found for NPB-based standard device B (maximum η_{ext}, η_L, brightness, and V_{on} of 1.3%, 4.0 cd/A, and 25 000 cd/m^2, and 2.3 V, respectively). The hole mobility of MTPC-Me determined by time-of-flight measurement is about 1.9×10^{-4} cm^2/V s, which is comparable to the value reported for NPB.

In device C, a 10-nm-thick BCP film was inserted between MTPC-Me and Alq_3 to prevent leaking excitons into the Alq_3 layer as BCP layer has a high HOMO level compared to Alq_3 and would block the passage of holes out of MTPC-Me. Device C gave a pure n-UV EL emission (λ_{max}, 396 nm) with a narrow FWHM of 40 nm, as shown in Fig. 5. The maximum η_{ext}, brightness, and V_{on} of device C are 1.2%, 1040 cd/m^2, and 3.5 V (Fig. 5), respectively, comparable to that found for CBP (Ref. 7) and TPD-based[8,9] n-UV OLEDs. Recently, a high-performance n-UV OLEDs with a high η_{ext} up to 3.6%. was reported by using 2,2″-bi-9,9′-spirobifluorene (B2).[10] However, the EL emission from this n-UV OLED extended into visible region (λ_{max} $\approx$425 nm) and its FWHM broadened to $\sim$70 nm. The V_{on} of device C was higher than that of device A or device B, this would be attributed to the LUMO level of MTPC-Me (−2.0 eV) at higher energy level than that of BCP (−2.9 eV), resulting in higher energy barrier for electrons to jump into the MTPC-Me layer. This barrier might be reduced by replacing BCP/Alq_3 with a HBM and ETM of (1,3,5-phenylene) tris(1-phenyl-1*H*-benzimidazole).[13]

In summary, a novel wide-band-gap 1,3,6,8-substituted carbazole derivative with a good thermal stability, a good hole-transporting property, and a stong n-UV emission was prepared and successfully used as an efficient n-UV EM and HTM in OLEDs. Given the fact that the molecular structure and, hence, the electronic properties of MTPC-Me and its derivatives could be varied, the development of high-performance n-UV OLEDs using this kind of compounds is envisaged. The present findings also suggest that MTPC-Me is a potential good host material in electrophosphorescence devices.

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